19 **Federal Republic of Germany**

12 **OLS**

11 **DE 32 43 194 A1**

21 Reference: P 32 43 194.5

43 Laid open to inspection on: 24. 5. 84

German Patent Office

51 Int. Cl. [3]:
C 08 L 83/04
C 08 K 3/36
C 08 K 5/14
C 08 K 5/64
C 08 J 3/24

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Request for examination was made based on § 44 Patent Law

54 Process for preparing silicone rubber vulcanizates

Silicone rubber mixture containing silicon dioxide is vulcanized by peroxides in the presence of polymethyl hydrogen siloxanes based on the formula

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Process for preparing silicone rubber vulcanizates

Claims

1. Process for Preparing Silicon Rubber Vulcanizates, characterized by vulcanizing silicone rubber containing silicon dioxide by means of peroxide in the presence polymethyl hydrogen siloxane.

2. Process based on Claim 1, characterized by adding the polymethylene hydrogen siloxane mixed with silicon dioxide to the mixture to be vulcanized.

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Process for Preparing Silicone Rubber Vulcanizates

It is well known how to vulcanize silicone rubber in the presence of peroxides (Noll, Chemie und Technologie der Silicone, publisher Chemie 1968, page 197 and DE-PS 11 62 560). However, the known processes result in more or less yellowed vulcanizates so that it is desirable to develop a process which does not result in yellowed vulcanizates.

The object of the invention is a process for preparing silicone rubber vulcanizates which is characterized by vulcanizing silicone rubber containing silicon dioxide by means of peroxide in the presence of polymethyl hydrogen siloxane. A compound of the formula may be used as polymethyl hydrogen siloxane

The amount of applied polymethyl hydrogen siloxane may amount to 0.1 to 2 wt.-%, preferably 0.6 wt-% with respect to the applied amount of rubber.

Precipitated silicon dioxide and/or silicon dioxide prepared pyrogenically may be used as silicon dioxide. It is also possible to use the silicon dioxide in the hydrophobic form.

In an advantageous embodiment of the invention the polymethyl hydrogen siloxane may be added to the mixture to be vulcanized, mixed with silicon dioxide. Here the amount of polymethylene hydrogen siloxane may range up to 10 wt.-% with respect to the applied amount of silicon dioxide.

One may use, for example, as peroxides:

dicumyl peroxide (95%)

bis-2,4-dichlorobenzoyl peroxide

However, it is also possible to use the following categories of peroxides: diaroyl peroxides such as dibenzoyl peroxide, di-p-chlorobenzoyl peroxide, bis-2,4-dichlorobenzoyl peroxide, di-alkyl peroxides such as di-tert. butyl peroxide, diaralkyl peroxide such as dicumyl peroxides as well as alkylaryl peroxides, alkylarayl and alkylacyl peroxides such as tert. butyl perbenzoate or tert. butyl peracetate and/or mixtures of replacements of various categories such as dibenzoyl peroxide and tert. butyl perbenzoate.

One may use preferably as silicone rubber a polydimethyl siloxane containing vinyl groups end-blocked with trimethyl siloxyl groups as described in DE-OS 29 11 352, Example 1.

The process of the invention produces the advantage that the vulcanizate does not have any undesirable yellowing.

Examples

The applied polymers A or B [is] a polydimethyl siloxane which has vinyl groups end-blocked with trimethyl siloxyl groups.

Baysilon®-öl [oil] MH 15 is used as polymethylene hydrogen. It corresponds to the indicated formula in which n = 40.

The applied silicic acids have the following physical-chemical characteristic data:

	BET Surface	Average size of primary particles	Loss on ignition	Carbon	pH value	First method [?]
	[m^2/g]	[nm]	[%]	[%]		
Aerosil 380	380	7	<2.5	-	3.9	pyrogen
R 972/300	250	7	<2	1	3.6	pyrogen
FK 320 DS	170	18	5	-	6.3	precipitation
FK 160	160	18	3.3	-	4.5	precipitation
VP D 15	110	18	5.5	2.5	7.5	precipitation

Test Numbers 1 - 2

The polydimethyl siloxane A containing vinyl groups is mixed on mixing rolls with 0.6 phr (phr = parts per 100 parts of the resin = parts/100 parts of polymer) dicumyl peroxide. The pre-mixing is divided and half is mixed with 1% polymethyl hydrogen siloxane.

Sheets 6 mm thick from both mixtures are vulcanized in a heatable press at 180°C with a vulcanization duration of 15 minutes. The silicon rubber sheets are then placed for 6 hours at 200°C in the circulating air-oven.

With the help of a color measuring device (RFC 3 from Zeis) the standard colored values X, Y, Z are determined with the specimens produced in this way. (Standard light type D 65, 10° standard observer.) The yellowing value and the yellowing number were calculated from these measurement results based on DIN 6167:

$$= \frac{1.301\ x - 1.149\ z}{Y} \bullet 10 \text{ and } V = C_b - Cu$$

Test numbers		1	2	3	4	5	6	7	8	9	10
Dimethyl polysiloxane A	Parts	100	100	100	100	100	100	100	100	100	100
Polymethyl hydrogen siloxane	"	-	1	-	1.4	-	1.4	-	1	-	2.8
Silicic acid VP D15	"	-	-	35	35	-	-	-	-	-	-
Silicic acid FK 160	"	-	-	-	-	40	40	-	-	-	-
Silicic acid FK 320 DS	"	-	-	-	-	-	-	-	-	40	40
Dicumyl peroxide	"	0.6	0.6	0.81	0.81	0.84	0.84	-	-	-	-
bis-2,4-dichlorobenzoyl peroxide	"	-	-	-	-	-	-	0.5	0.5	0.7	0.7
Yellowing value		19	-5	85	43	73	38	-5	-5	40	18
Yellowing number		"0"	-24	"0"	-42	"0"	-35	"0"	±0	"0"	-22
Standard color value X		63	67	22	36	28	40	70	72	27	36
Standard color value Y		68	70	21	37	27	41	74	75	28	38
Standard color value Z			61	79	10	27	14	31	83	84	21 35

Table 1 (continued)

Test numbers		1	2	11	12	13	14
Dimethyl polysiloxane A	Parts	100	100	100	100	100	100
Polymethyl hydrogen siloxane	"	-	1	-	0.4	0.8	1.2
Aerosil R 972/300	"	-	-	40	40	40	40
Dicumyl peroxide	"	0.6	0.6	0.85	0.85	0.85	0.85
Yellowing value G		19	-5	65	47	39	36
Yellowing number		"0"	-24	"0"	-18	-26	-29
Standard color value X		63	67	39	43	45	46
Standard color value Y		68	70	41	45	47	48
Standard color value Z			61	79	22	30	35 37

Table 3 (sic)

Test numbers	15	16	17	18	19

Dimethyl polysiloxane B	Parts	100	100	100	100	100	
Polymethyl hydrogen siloxane	"	-	-	1	-	1.4	
Aerosil 380	"	-	-	-	35	35	
Dicumyl peroxide	"	-	0.6	0.6	0.8	0.8	
Bis-2,4-dichlorobenzoyl peroxide*	"	0.5	-	-	-	-	
Yellowing value G		8	44	13	61	24	
Yellowing number V		-	"0"	-31	"0"	-37	
Standard color value X		63	59	64	43	50	
Standard color value Y		67	63	68	45	52	
Standard color value Z			67	42	65	25	45